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THERMODYNAMIC ANALOGIES FOR A SIMPLE DYNAMICAL SYSTEM

BY EDWIN BIDWELL WILSON

Introduction. IN a recent article * I have set forth some of the most elementary notions in regard to the statistical mechanics of dynamical systems. The object of the present communication, which may be regarded as a sequel to the other, is to investigate a simple dynamical system for the purpose of exhibiting certain analogies between its statistical properties and the elementary thermodynamics of gases. The dynamical system which I shall choose is the somewhat familiar household article known as the Japanese or Chinese dinner-gong and consisting of a series of gongs of varying sizes suspended one above another upon a vertical string. The number of degrees of freedom of a set of several gongs is considerable; and to simplify the work it will be assumed that the only motion which the gongs may have is one of rotation about the vertical string as axis. Under this hypothesis the number of degrees of freedom will be equal to the number of gongs in the set.

To find the equations of motion of the system in the Lagrangian or Hamiltonian form, it is first necessary to write down the kinetic and potential energies of the system. If $I_1, I_2, I_3, \cdots$ are the moments of inertia of the successive gongs beginning with the top one and if $q_1, q_2, q_3, \cdots$ are the angles through which the respective gongs have turned from the position of equilibrium in which there is no twist in any of the strings, the angular velocities of the gongs will be respectively $\dot{q}_1, \dot{q}_2, \dot{q}_3, \cdots$ and the kinetic energy of the system will be

$$T = \tfrac{1}{2}(I_1\dot{q}_1^2 + I_2\dot{q}_2^2 + I_3\dot{q}_3^2 + \cdots).$$

The momenta corresponding to the different coordinates are

$$p_i = \frac{\partial T}{\partial \dot{q}_i} = I_i\dot{q}_i \qquad \text{or} \qquad \dot{q}_i = \frac{p_i}{I_i};$$

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* Applications of Probability to Mechanics, ANNALS OF MATHEMATICS, volume 10, pp. 129–148 (1909). References to this article will be given simply by the page numbers in parentheses without the quotation of the title.

and hence as a function of the momenta the kinetic energy is

$$T = \epsilon_p = \tfrac{1}{2}\left(\frac{p_1^2}{I_1} + \frac{p_2^2}{I_2} + \frac{p_3^2}{I_3} + \cdots\right).^*$$

For the purpose of getting rid of the constant π in some of the subsequent averages, the assumption will be made that the product

$$I_1 I_2 I_3 \cdots = \frac{1}{2\pi},$$

and the kinetic energy will be taken in the form

$$T = \epsilon_p = \pi(a_1 p_1^2 + a_2 p_2^2 + a_3 p_3^2 + \cdots), \qquad a_1 a_2 a_3 \cdots = 1. \tag{1}$$

The potential energy of the system will consist of the energies stored in the twisted strings. The twists in the successive strings beginning with the top one and running down are

$$q_1,\ q_2 - q_1,\ q_3 - q_2,\ \cdots.$$

The potential energy will be proportional to the square of the twist, where the factor of proportionality may depend on a variety of things such as the kind of string, the diameter of the string, the length of the string, and the tension in the string due to the weight of the gongs. In order that there may be some possible variation of the system as a whole it will be assumed that the length of the uppermost string is adjustable; this could easily be arranged by running the string between two closely pressed wheels, which could be moved up and down along the string, instead of merely pinching it in a vice. It is then important to know at least how the factor of proportionality varies with the length of a uniform string when nothing but the length changes. Now. from the symmetry of the figure it appears that to twist a string through an angle q is equivalent to twisting each half of it through the angle $\frac{1}{2}q$ in opposite directions. Hence if the factor of proportionality is supposed to vary with the nth power of the length and is written as kl^n, the equation of the whole potential energy to the energy of the two halves gives

$$kl^n q^2 = 2k\left(\frac{l}{2}\right)^n\left(\frac{q}{2}\right)^2 \qquad \text{or} \qquad 1 = \tfrac{1}{2}\left(\frac{1}{2}\right)^n$$

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[*] The use of ϵ_p for kinetic energy, ϵ_q for potential energy, and $\epsilon = T + V = \epsilon_p + \epsilon_q$ for total energy is adopted to conform to the usages of Gibbs's *Elementary Principles in Statistical Mechanics*.

and it is seen that $n = -1$. The potential energy of the system will therefore be written in the form

$$V = \epsilon_q = k_1 l_1^{-1} q_1^2 + k_2 l_2^{-1}(q_2 - q_1)^2 + k_3 l_3^{-1}(q_3 - q_2)^2 + \cdots.$$

For the sake of simplification let it be assumed that an adjustment between the sort of string and the diameter of the strings and the units of measurement has been made so that

$$k_2 l_2^{-1} = \pi, \quad k_3 l_3^{-1} = \pi, \cdots; \quad \text{and let} \quad k_1 l_1^{-1} = \pi v^{-4},$$

so that the parameter v is proportional to the fourth root of the length of the uppermost string of variable length. Then

$$V = \epsilon_q = \pi[v^{-4} q_1^2 + (q_2 - q_1)^2 + (q_3 - q_2)^2 + \cdots]$$

is the expression for the potential energy of the system.

The differential equations for the motion would be

$$\dot{p}_1 + (v^{-4} + 1) q_1 - q_2 = 0, \quad \dot{p}_2 + 2q_2 - q_1 - q_3 = 0, \cdots$$

or

$$\dot{p}_1 + (v^{-4} + 1) q_1 - q_2 = 0, \quad \dot{q}_1 = a_1 p_1, \quad \dot{p}_2 + 2q_2 - q_1 - q_3 = 0, \quad \dot{q}_2 = a_2 p_2, \cdots$$

by direct substitution in the formulas of the Lagrangian or Hamiltonian equations (see page 147), where

$$T - V = \epsilon_p - \epsilon_q = \pi[a_1 p_1^2 + a_2 p_2^2 + a_3 p_3^2 + \cdots - v^{-4} q_1^2 - (q_2 - q_1)^2 - (q_3 - q_2)^2 \cdots]$$

or

$$T + V = \epsilon_p + \epsilon_q = \pi[a_1 p_1^2 + a_2 p_2^2 + a_3 p_3^2 + \cdots + v^{-4} q_1^2 + (q_2 - q_1)^2, + (q_3 - q_2)^2 + \cdots].$$

If D denotes differentiation with respect to the time, the Hamiltonian equations after the elimination of the momenta are

$$\left[\frac{1}{a_1} D^2 + (v^{-4} + 1)\right] q_1 - q_2 = 0,$$

$$-q_1 + \left[\frac{1}{a_2} D^2 + 2\right] q_2 - q_3 = 0,$$

$$\cdots\cdots\cdots\cdots\cdots\cdots\cdots$$

Hence, if for example the number of gongs is three, the solution of the differential equations* depends on the solution of

$$\begin{vmatrix} \frac{1}{a_1}D^2 + v^{-4} + 1 & -1 & 0 \\ -1 & \frac{1}{a_2}D^2 + 2 & -1 \\ 0 & -1 & \frac{1}{a_3}D^2 + 1 \end{vmatrix} = 0,$$

which is an algebraic equation of the third degree in D^2. If there had been five gongs the solution would have depended on the solution of an algebraic equation of the fifth degree in D^2. As these equations are necessarily literal when the length of the uppermost string is adjustable and v cannot be assigned a numerical value, the solution of the algebraic equations is impossible in practice. This will make no difference to us inasmuch as the discussion of statistical mechanics is based on the differential equations and not upon their integrals.

1. The canonical distribution. Suppose for the moment that the system consists of three gongs. The state of the system is at any instant completely determined by the values of the six quantities $q_1, q_2, q_3, p_1, p_2, p_3$. The representative point of the motion would therefore be located in a space of six dimensions. Consider an ensemble of these dinner-gong systems distributed with the density or better with the probability (see page 148)

$$P = e^{\frac{\psi - \epsilon}{\Theta}}, \quad \epsilon = T + V = \epsilon_p + \epsilon_q, \quad \psi \text{ and } \Theta \text{ constant,}$$

where

$$\epsilon = \pi \left[a_1 p_1^2 + a_2 p_2^2 + a_3 p_3^2 + v^{-4} q_1^2 + (q_2 - q_1)^2 + (q_3 - q_2)^2\right].$$

The distribution will be in statistical equilibrium because the probability, or density which is proportional to it, is a function of the energy alone and the energy is an invariant of the motion. Let it further be assumed that the distribution covers the whole of the six-dimensional representative space so that the relation

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* See Forsyth's *Differential Equations*, 3rd edition, p. 305. Or Cohen's *Differential Equations*, p. 150. Or any treatment of simultaneous linear differential equations with constant coefficients.

$$\int\int\int_{-\infty}^{+\infty}\int\int\int e^{\frac{\psi-\epsilon}{\Theta}} dp_1 dp_2 dp_3 dq_1 dq_2 dq_3 = 1 \tag{2}$$

must be satisfied (see pages 132, 142). This distribution will be considered as the *canonical* distribution and averages over it will be investigated.*

The equation (2) may be used to determine the constant ψ in terms of the other constants of the problem. For as ψ and Θ are constants, the factor $e^{\frac{\psi}{\Theta}}$ may be passed out from under the sign of integration and may be transferred to the other side of the equation. Then

$$e^{-\frac{\psi}{\Theta}} = \int\int\int_{-\infty}^{+\infty}\int\int\int e^{-\frac{\epsilon}{\Theta}} dp_1 dp_2 dp_3 dq_1 dq_2 dq_3 =$$

$$\int_{-\infty}^{+\infty} e^{-\frac{\pi p_1^2}{a_1\Theta}} dp_1 \int_{-\infty}^{+\infty} e^{-\frac{\pi p_2^2}{a_2\Theta}} dp_2 \int_{-\infty}^{+\infty} e^{-\frac{\pi p_3^2}{a_3\Theta}} dp_3 \times$$

$$\int_{-\infty}^{+\infty} e^{-\frac{\pi q_1^2}{v^4\Theta}} dq_1 \int_{-\infty}^{+\infty} e^{-\frac{\pi (q_2-q_1)^2}{\Theta}} dq_2 \int_{-\infty}^{+\infty} e^{-\frac{\pi (q_3-q_2)^2}{\Theta}} dq_3.$$

Here the six successive integrations are to be carried out by beginning with the one for q_3 and working backward through the list. As q_2 is regarded as constant for the integration with respect to q_3, we may write

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* As a general comment on the assumptions underlying the foregoing use of a canonical distribution, one point in particular should be mentioned. It has been assumed that the representative points for the motion of the systems in the ensemble are spread over the whole of the representative space, that is, that the coordinates $q_1, q_2, q_3, \ldots$ and momenta $p_1, p_2, p_3, \ldots$ may have any value. This necessitates the admission that the angular velocities of the discs and the twists in the strings may be indefinitely great. It goes without saying that this is physically impossible: for if the strings were allowed to twist very much, the law of torsion would depart from the simple linear (Hooke's) law and the expression of the potential energy would change; furthermore the twisting would perhaps materially shorten the strings and introduce complications on that score. It should be noted, however, that as the coordinates and momenta increase, the energy increases with their square, and the probability assumed for the distribution decreases exponentially with the energy. Hence the probabilty of systems with large velocities and twists is almost negligibly small compared with that of systems with small velocities and twists. The errors made by entirely neglecting the systems in which the velocities or twists were so large as to introduce physical difficulties would therefore probably be small and could certainly be made small by restricting Θ to sufficiently small values. Hence there is no need of worrying very much over such difficulties.

$$\int_{-\infty}^{+\infty} e^{-\frac{\pi(q_3-q_2)^2}{\Theta}}\,dq_3=\int_{-\infty}^{+\infty} e^{-\frac{\pi(q_3-q_2)^2}{\Theta}}\,d(q_3-q_2)=\frac{\sqrt{\Theta}}{\sqrt{\pi}}\,\sqrt{\pi}=\sqrt{\Theta}.$$

The result is independent of q_2; in fact the integrals may be regarded as multiplied instead of iterated. The result is

$$e^{-\frac{\psi}{\Theta}}=\sqrt{a_1a_2a_3}\;v^2(\sqrt{\Theta})^6=v^2\Theta^3,$$

the last reduction being due to the assumption (1). Hence

$$\psi=-2\,\Theta\log v-3\,\Theta\log\Theta. \tag{3}$$

It is readily seen that if there had been n gongs, the expression for ψ would have been

$$\psi=-2\,\Theta\log v-n\,\Theta\log\Theta. \tag{3$'$}$$

Another important quantity is the index η of probability which is defined as the logarithm of the probability. Thus

$$\eta=\log P=\frac{\psi-\epsilon}{\Theta},\qquad P=\epsilon^{\eta}.$$

The average value of the index of probability η taken over the ensemble is found by evaluating the integral

$$\bar{\eta}=\int_{-\infty}^{+\infty}\!\cdots\!\int\eta e^{\eta}dp_1\cdots dq_3.$$

This may be evaluated directly; but the work may be very much shortened by adopting the device of differentiating (2) with respect to Θ regarded as a parameter. Upon the left-hand side, the differentiation may by Leibniz's rule be carried under the sign of integration. The result is

$$\int_{-\infty}^{+\infty}\!\cdots\!\int\frac{\partial}{\partial\Theta}e^{\frac{\psi-\epsilon}{\Theta}}\,dp_1\cdots dq_3=\int_{-\infty}^{+\infty}\!\cdots\!\int\left[-\frac{\psi-\epsilon}{\Theta^2}+\frac{1}{\Theta}\frac{\partial\psi}{\partial\Theta}\right]e^{\frac{\psi-\epsilon}{\Theta}}\,dp_1\cdots dq_3=0.$$

Now Θ may be canceled out and the result transposed so that

$$\frac{\partial\psi}{\partial\Theta}\int_{-\infty}^{+\infty}\!\cdots\!\int e^{\frac{\psi-\epsilon}{\Theta}}\,dp_1\cdots dq_3=\int_{-\infty}^{+\infty}\!\cdots\!\int\frac{\psi-\epsilon}{\Theta}\,e^{\frac{\psi-\epsilon}{\Theta}}\,dp_1\cdots dq_3$$

or

$$\frac{\partial\psi}{\partial\Theta}\cdot 1=\int_{-\infty}^{+\infty}\!\cdots\!\int\eta e^{\eta}dp_1\cdots dq_3=\bar{\eta}.$$

That the factor $\partial\psi/\partial\,\Theta$ may be transferred to outside the integral sign depends on the fact that ψ in (3) does not contain the variables with regard to which the integration is performed.

By differentiating ψ with respect to Θ the value of $\bar{\eta}$ is

$$\bar{\eta} = -\,2\log v - 3\log\Theta - 3. \tag{4}$$

And now the average value $\bar{\epsilon}$ of the energy ϵ may be found very simply. For as ψ and Θ are constants, it follows from

$$\eta = \frac{\psi - \epsilon}{\Theta} \quad \text{that} \quad \bar{\eta} = \frac{\psi - \bar{\epsilon}}{\Theta}.$$

Hence

$$\bar{\epsilon} = \psi - \Theta\,\bar{\eta} = 3\Theta. \tag{5}$$

Moreover if there were n gongs, the results would be

$$\eta = -\,2\log v - n\log\Theta - n, \tag{4'}$$

$$\epsilon = \psi - \Theta\,\bar{\eta} = n\,\Theta. \tag{5'}$$

The parameter v which enters into the expression for the potential energy and which determines the length of the uppermost string may be regarded as an external coordinate of the system. The difference between an external and an internal coordinate is simply that the internal coordinates are those which take an active part in the motion, and in the solution are to be expressed in terms of the time; whereas the external coordinates fix the system as a whole and take no active part in the motion, although different motions will arise from varying such coordinates. Now the forces are derivable from the potential energy and they will be of two sorts, internal and external. If $Q_1, Q_2, Q_3, \cdots$ are the internal forces and A is the external force,* then

$$Q_1 = -\frac{\partial\epsilon_q}{\partial q_1}, \quad Q_2 = -\frac{\partial\epsilon_q}{\partial q_2}, \cdots, \quad A = -\frac{\partial\epsilon_q}{\partial v}.$$

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* The external force A should not be confused with the force which is required to support the system of gongs from falling under the influence of gravity. The force of gravity does not enter essentially into our problem. In fact it might be convenient to imagine that the force of gravity were continuously diminished toward zero as a limit as if the system were removed to a point indefinitely near to center of the earth. It may be noted, however, that the force of gravity does no work on the system even when the length of the uppermost string is changed: for the assumption has been made that the wheels which pinch the string are moved up and down to regulate the length rather than that the string should be paid out between them in such a way as to raise or lower the system.

It is easy to see without recourse to formulas that if the uppermost string is lengthened, the system loses energy: for a given angular twist upon a short string represents a greater amount of energy stored in the string than does the same twist in a longer string.

The average value of the external force A over the ensemble may readily be computed. It is merely

$$\bar{A} = \int_{-\infty}^{+\infty} \cdots \int -\frac{\partial \epsilon_q}{\partial v} e^{\frac{\psi - \epsilon}{\Theta}} dp_1 \cdots dq_3.$$

To evaluate this the device of differentiating (2) will again be used, but in this case the differentiation will be with respect to v. Note that ψ contains v but Θ does not, and that as ϵ_p does not contain v, the derivatives of ϵ and ϵ_q with respect to v are equal. Then

$$\int_{-\infty}^{+\infty} \cdots \int \frac{1}{\Theta}\left(\frac{\partial \psi}{\partial v} - \frac{\partial \epsilon_q}{\partial v}\right) e^{\frac{\psi - \epsilon}{\Theta}} dp_1 \cdots dq_3 = 0,$$

$$\bar{A} = \int_{-\infty}^{+\infty} \cdots \int -\frac{\partial \epsilon_q}{\partial v} e^{\eta} dp_1 \cdots dq_3 = -\frac{\partial \psi}{dv} \int_{-\infty}^{+\infty} \cdots \int e^{\eta} dp_1 \cdots dq_3.$$

Hence

$$\bar{A} = -\frac{\partial \psi}{\partial v} \cdot 1 = 2\,\frac{\Theta}{v}. \tag{6}$$

The result is independent of the number of gongs.

2. A thermodynamic analogy. Let p, V, T, U, S be respectively the pressure, volume, temperature, energy, and entropy of a gas. Let the gas be assumed to be in so far perfect or ideal as to satisfy Boyle's characteristic equation $pV = RT$ without sensible error. Further let the units of measurement be those ordinarily adopted in theoretical and practical physical chemistry.* Then $pV = 2T$ is the form of the characteristic equation. Moreover the energy of a perfect gas varies directly with the absolute temperature and is $U = c_v T$ where c_v denotes the specific heat at constant volume. In the

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* At the absolute temperature $T = 273^\circ$ centigrade of melting ice and under the normal atmospheric pressure of 76 cm. of mercury or 1033 gr. per sq. cm., the gram-molecular volume is 22,380 cu. cm. Hence

$$R = \frac{1033 \times 22380}{273 \times 42350} = 2 \quad \text{(or just a trifle less).}$$

See Walker's *Introduction to Physical Chemistry*, 2nd edition, p. 30, or any similar work.

physico-chemical system of units $c_v = 3$ for a monatomic gas; for the ordinary diatomic gas $c_v = 5$; and for more complicated gases the values are 6, 7, 8 or numbers in the immediate vicinity of these integers.* Hence there is the equation

$$U = c_v T = nT, \qquad n = 3, 5, 6, 7, 8,$$

for the energy of any ordinary simple perfect gas. The entropy and free energy of the gas have the familiar forms

$$S = c_v \log T + 2 \log V + \text{const.} \quad \text{and} \quad \psi = -2T \log V - c_v T \log T;$$

and finally, the thermodynamic surface for the gas, which is the equation between the energy, entropy and volume, is

$$U^{c_v} V^2 = Ke^S, \qquad K \text{ an arbitrary const.}$$

With these data for gases in mind it is easy to set up an analogy between the thermodynamics of a perfect gas and the averages obtained over a canonically distributed ensemble of vibrating dinner-gongs. The results may be exhibited most graphically in double columns.

Thermodynamics of a Perfect Gas	*Statistical Mechanics of the Dinner-gong*
temperature T	constant (modulus) Θ
energy U	average energy $\bar{\epsilon}$
entropy S	negative average index of probability $-\bar{\eta}$
free energy ψ	constant ψ
volume V	external coordinate $v \propto l^{\frac{1}{4}}$
pressure $p = -\left(\frac{\partial \psi}{\partial V}\right)_T$	average external generalized force $\bar{A} = -\left(\frac{\partial \psi}{\partial v}\right)_\Theta$
specific heat c_v	degrees of freedom n
equation $pV = 2T$†	equation $\bar{A}v = 2\Theta$

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* These numbers are of course the "degrees of freedom" of the molecule. Chlorine is a somewhat anomolous diatomic gas with $c_v = 6$. Ethylene give $c_v = 8$.

† This is the so-called characteristic equation of Boyle for perfect gases.

equation $U = c_v T$	equation $\bar{\epsilon} = n\Theta$
equation $\psi = -2T\log V - c_v T\log T$	equation $\psi = -2\Theta\log v - n\Theta\log\Theta$
equation $S = c_v \log T + 2\log V + \text{const.}$*	equation $-\bar{\eta} = n\log\Theta + 2\log v + n$
equation $U^{c_v} V^2 = Ke^S$†	equation $\bar{\epsilon}^n v^2 = k\, e^{-\bar{\eta}}$

It therefore appears that the statistical mechanics of the system containing n gongs has all the formal properties of the thermodynamics of a perfect gas except that the arbitrary constant which enters into the entropy of a gas (and consequently into certain other formulas) is determined in the dynamical system. It may be well to note in particular some of the correspondences. The volume of the gas is related with the fourth root of the length of the uppermost string. If the volume is increased, the gas does work and loses energy; if the string is lengthened energy is lost to the system. To the specific heat corresponds the number of gongs, that is, the number of degrees of freedom in the system—and this is precisely the number of degrees of freedom assigned to the molecules of the gas. As the above equations contain the basis of all the thermodynamics of the gas and have identical analogs in the averages taken over the canonically distributed ensemble of dynamical systems, it appears that the development of the two could never diverge. This conclusion, however, is a bit hasty for the reason that nothing has been developed which is analogous to the mixing of two gases. As a matter of fact the mixing of gases depends on a principle in addition to those here given for a simple gas and contains a somewhat troublesome paradox known as Gibbs's paradox. The matter of mixing gases and the analogous combinations of dynamical systems will therefore be omitted from the present discussion.

There is one point of general import which should be mentioned. The reason for replacing the study of one particular vibrating system of gongs by the study of average values over an ensemble was that nothing was supposed to be known concerning the initial conditions of any one system (page

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* The entropy necessarily contains an additive constant as it is defined by an integral for which there is no natural lower limit — the absolute zero of temperature being excluded because the integral diverges for $T = 0$. Similarly $\psi = U - TS$ contains an arbitrary constant and may be written $\psi = -2T\log V - c_v T\log T + (c_v - \text{const.})\ T$; but the origin of entropy may be so chosen as to make this final term vanish. The constant n which occurs in $-\bar{\eta}$ is not arbitrary.

† The equation of the thermodynamic surface. The constant K is arbitrary owing to he additive constant in S; but $k = e^{-n}$.

137–8); the only known fact was the total energy of the system and the differential equations of motion immediately derivable therefrom. The question naturally arises: How nearly do the average values represent the conditions likely to obtain in a system selected at random? This is quite like the analogous question in the theory of errors of observation: How reliable is the result as determined by the theory? A measure of the reliability of the result is assumed to be found in the value of the mean square error; and for the dynamical systems the average value of the square of the departure $\epsilon - \bar{\epsilon}$ of the energy from its mean value may naturally be taken as a measure of how far the average state differs from the state of a system selected at random. It remains, therefore to evaluate the average of $(\bar{\epsilon} - \epsilon)^2$.

Now it is clear that the relations

$$\overline{(\epsilon - \bar{\epsilon})^2} = \overline{\epsilon^2 - 2\epsilon\bar{\epsilon} + \bar{\epsilon}^2} = \overline{\epsilon^2} - 2\bar{\epsilon}\bar{\epsilon} + \bar{\epsilon}^2 = \overline{\epsilon^2} - \bar{\epsilon}^2$$

hold for the averages. It is therefore necessary to evaluate $\overline{\epsilon^2}$; and the device of differentiating under the sign of integration may again be advantageously employed. By definition and by (5) we have

$$\bar{\epsilon} = \int_{-\infty}^{+\infty}\cdots\int \epsilon e^{\frac{\psi - \epsilon}{\Theta}}\, dp_1 \cdots dq_3 = 3\Theta.$$

Now differentiate with respect to Θ on both sides. Then

$$\int_{-\infty}^{+\infty}\cdots\int - \epsilon\left[\frac{\psi - \epsilon}{\Theta^2} - \frac{1}{\Theta}\frac{\partial\psi}{\partial\Theta}\right] e^{\frac{\psi - \epsilon}{\Theta}}\, dp_1 \cdots dq_3 = 3.$$

or
$$\int_{-\infty}^{+\infty}\cdots\int \epsilon^2 e^{\frac{\psi - \epsilon}{\Theta}}\, dp_1 \cdots dq_3 - \psi \int_{-\infty}^{+\infty}\cdots\int \epsilon e^{\frac{\psi - \epsilon}{\Theta}}\, dp_1 \cdots dq_3$$
$$+ \Theta\frac{\partial\psi}{\partial\Theta}\int_{-\infty}^{+\infty}\cdots\int \epsilon e^{\frac{\psi - \epsilon}{\Theta}}\, dp_1 \cdots dq_3 = 3\Theta^2.$$

or
$$\overline{\epsilon^2} - \psi\,\bar{\epsilon} + \Theta\frac{\partial\psi}{\partial\Theta}\,\bar{\epsilon} = 3\Theta^2.$$

The substitution from (5) and (3) or from (5′) or (3′) gives

$$\overline{\epsilon^2} = 12\Theta^2 \quad \text{or} \quad n(n+1)\Theta^2; \quad \overline{\epsilon^2} - \bar{\epsilon}^2 = 3\Theta^2 \quad \text{or} \quad n\Theta^2,$$

according as the number of gongs is 3 or n. Hence the ratio

$$\overline{(\epsilon-\bar{\epsilon})^2} : \bar{\epsilon}^2 = 1:3 \quad \text{or} \quad 1:n.$$

It therefore appears that as far as the energy is concerned, the mean square error in assuming that the average represents a system selected at random is considerable when n is small but not very large when n is great and becomes quite negligible when n is very great. A similar calculation could be carried out for the quantities

$$\overline{(\eta-\bar{\eta})^2} \qquad \text{and} \qquad \overline{(A-\bar{A})^2};$$

but this will be left to the reader.

A simple device will give a system in which the average condition better represents the condition probably found in a system selected at random. For suppose that instead of considering single sets of n gongs, the attention is turned toward pairs of exactly similar sets or in general to a system consisting of N of the single systems of gongs. This compound system will have Nn degrees of freedom if each individual set has n gongs. The energy of the compound system will be

$$\epsilon = \sum_1^N \epsilon_i = \pi \sum_1^N$$

$$\left[a_1 p_{1i}^2 + p_{2i}^2 + p_{3i}^2 + \cdots + v^{-4} q_{1i}^2 + (q_{2i}-q_{1i})^2 + (q_{3i}-q_{2i})^2 + \cdots\right].$$

If the compound systems are to be canonically distributed over their representative space of $2Nn$ dimensions, the probability will be $e^{\frac{\psi-\epsilon}{\Theta}}$ where ϵ has this new value. As there are no relations between the different sets of coordinates and momenta $p_{1i}, p_{2i}, p_{3i}, \cdots, q_{1i}, q_{2i}, q_{3i}, \cdots$, it is readily seen that the quantities connected with the compound systems are

$$\psi = -\,2N\,\Theta \log v - Nn\,\Theta \log \Theta$$

$$\bar{\eta} = \frac{\partial\psi}{\partial\Theta} = -\,2N \log v - Nn \log \Theta - Nn$$

$$\bar{\epsilon} = \psi - \Theta\bar{\eta} = Nn\Theta$$

$$\bar{A} = -\frac{\partial\psi}{\partial v} = 2N\,\frac{\Theta}{v}, \qquad \bar{A}v = 2N\Theta$$

$$\overline{(\epsilon-\bar{\epsilon})^2} : \bar{\epsilon}^2 = 1 : Nn$$

By taking N sufficiently large, the probability of the energy of an arbitrarily selected system being noticeably at variance with the average energy is very small. Moreover the only difference between the new and the old equations is that ψ, $\bar{\eta}$, $\bar{\epsilon}$, $\bar{A}$, are multiplied by the constant N — a difference which is of the same sort as if these quantities were measured in different units. The thermodynamic analogy therefore persists in all its essentials. It even has an additional advantage in that now any one system represents the average or vice versa with great probable precision, which is surely true of any particular sample of gas and the average of all similar samples.

3. Microcanonical ensembles. A microcanonical distribution is derived from the canonical by confining the attention to those systems of the ensemble which are characterized by representative points between the surfaces $\epsilon = C$ and $\epsilon + d\epsilon = C + dC$ in the representative space. Now as the probability depends only on the energy and the energy is sensibly constant between these two surfaces, it follows that the actual infinitesimal probability (see page 134) that the representative point shall lie between the two successive surfaces is

$$PdV = e^{\frac{\psi - \epsilon}{\Theta}}\, dV = e^{\frac{\psi - \epsilon}{\Theta}} \left(\frac{dv}{d\epsilon}\right)_v^{*} d\epsilon,$$

where V represents the volume of the six-dimensional space included by the surface $\epsilon = C$ —a quadric surface in p_1, p_2, p_3, q_1, q_2, q_3, —and dV represents the increment of volume between this surface and the succeeding one.

It is necessary to calculate the volume

$$V = \int_{\epsilon = 0}^{\epsilon = C} \cdots \int dp_1 dp_2 dp_3 dq_1 dq_2 dq_3$$

within the ellipsoid $\epsilon = C$, where for definiteness and simplicity the problem has been restricted to the case of the single system consisting of only three gongs which is the case first handled in the previous discussion. The easiest way of evaluating V is to make the change of variable

$$x_1 = \sqrt{\pi a_1}\, p_1, \quad x_2 = \sqrt{\pi a_2}\, p_2, \quad x_3 = \sqrt{\pi a_3}\, p_3, \quad x_4 = \sqrt{\pi}\, v^{-2} q_1, \quad x_5 = \sqrt{\pi}(q_2 - q_1)$$

$$x_6 = \sqrt{\pi}(q_3 - q_2), \quad dp_1 \cdots dq_3 = \frac{v^2}{\pi^3} dx_1 \cdots dx_6 .^{\dagger}$$

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[*] As a system with a definite length for the uppermost string is under discussion, the quantity v is supposed to be constant at this point; later it will be allowed to vary.

[†] It may be recalled that to find the new element of volume when changing the variable in a multiple integral the Jacobian is introduced.

The integral to be evaluated then takes the form

$$V = \frac{1}{\pi^3 v^2} \int_{\epsilon = 0}^{\epsilon = C} \cdots \int dx_1 dx_2 dx_3 dx_4 dx_5 dx_6,$$

where $$x_1^2 + x_2^2 + x_3^2 + x_4^2 + x_5^2 + x_6^2 \leqq C.$$

This is a classic integral evaluable by means of the Γ— functions. The result is *

$$V = \frac{v^2}{\pi^3} \frac{[\Gamma(\frac{1}{2})]^6}{\Gamma(3)} \int_0^C h^2 dh = \tfrac{1}{6}\, C^3 v^2 = \tfrac{1}{6}\, \epsilon^3 v^2. \tag{7}$$

Now the expression for the probability may be written

$$P d V = e^{\frac{\psi - \epsilon}{\Theta}} \cdot \frac{1}{2} \frac{\epsilon^2}{v^2}\, d\epsilon\,;$$

and may be given a more convenient form by letting

$$\phi = \log\left(\frac{dV}{d\epsilon}\right)_v = 2 \log \epsilon - 2 \log v - \log 2,$$

so that $$P d V = e^{\frac{\psi - \epsilon}{\Theta} + \phi}\, d\epsilon \quad \text{and} \quad \int_0^\infty e^{\frac{\psi - \epsilon}{\Theta} + \phi}\, d\epsilon = 1,$$

the last condition being the new form of (2).

Now a second thermodynamic analogy may be set up. This time the analogy is between the quantities arising in the theory of a perfect gas and the average taken over a microcanonical ensemble. Equation (7) may be written as

$$\epsilon^3 v^2 = k e^{\log V} \quad \text{and compared with} \quad U^3 V^2 = K e^S.$$

It is then seen that the following are analogical:

In the Ensemble	*In the Gas*
the energy ϵ	the energy U
the quantity v	the volume V
the quantity $\log V$	the entropy S

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* See Todhunter's *Integral Calculus*, p. 263, article 278.

The list may be further extended by the use of the fundamental thermodynamic formula

$$d\epsilon = dH - p\,dV = T\,dS - p\,dV$$

compared with the result of differentiating ϵ, namely,

$$d\epsilon = \left(\frac{\partial \epsilon}{\partial \log V}\right)_v d\log V + \left(\frac{\partial \epsilon}{\partial v}\right)_{\log V} dv = e^{-\phi}\,V d\log V + \left(\frac{\partial \epsilon}{\partial v}\right)_{\log V} dv.$$

Then the following correspondences may be set up:

In the Ensemble	*In the Gas*
$\left(\frac{\partial \epsilon}{\partial \log V}\right)_v = e^{-\phi}\ V = \frac{1}{3}\epsilon$	the temperature T
$-\left(\frac{\partial \epsilon}{\partial v}\right)_{\log V} = \frac{2\epsilon}{3v} = A$	the pressure p
Equation $Av = 2e^{-\phi}\ V$	Equation $pV = 2T$

There seems to be no need to carry the table further. Similar results could have been found for the system with n gongs.

This second analogy has the distinct advantage that the energy of the dynamical system corresponds to the energy of the gas, whereas in the earlier analogy it was the average energy over the whole ensemble which corresponded to the energy of the gas. This is not the place and the necessary fine distinctions between closely related ideas in the theory of probability have not been sufficiently set forth to enter profitably into the discussion of the relative merits of the two analogies. On the whole, physicists seem to prefer the second, apparently mainly for the reason that the correspondence of the energies seems to them more natural; but Gibbs evidently inclined rather to prefer the first and to feel that (in view perhaps of the facts that for systems of so many degrees of freedom as a gas the energy of any one system could scarcely be expected to differ appreciably from the average energy and that we really do not know what the energy of the gas as a dynamical system is except in so far as it makes itself felt through the sort of average phenomena of pressure and temperature) the first correspondence was quite satisfactory; there are, moreover, some other reasons why it is more satisfactory.

Conclusion. The foregoing simple dynamical system in which the computations of finding averages have been so easy as to be carried out without difficulty and for which the thermodynamic analogies are immediately comparable with the ordinary theory of gases has been treated as far as possible in parallel with the general discussion of statistical mechanics given by J. Willard Gibbs in his *Elementary Principles in Statistical Mechanics*. That the simple and concrete case may perhaps be useful as an introduction to the general and abstract presentation of the statistical mechanics of any system which satisfies the Hamiltonian equations of motion is its only excuse for existence. There are, however, a number of matters which suggest themselves in connection with the foregoing work and with statistical mechanics in general which may deserve a moment's notice.

In the first place it might be considered remarkable that a system so simple and so apparently unlike a gas should give the thermodynamical equations of a gas. A reference to Gibbs's work will show, however, that the fundamental differential equation of thermodynamics and the fundamental equation of statistical mechanics

$$dU = TdS - pdV \quad \text{and} \quad d\bar{\epsilon} = \Theta d(-\bar{\eta}) - \bar{A}dV \quad \text{or} \quad d\epsilon = \epsilon^{-\phi} Vd \log V - Adv,$$

whether in the canonical or microcanonical ensemble, will always correspond when there is only one variable external coordinate in the system. It therefore only remains to select the dynamical system in such a way as to give the proper special results for a gas, namely, the characteristic equation, the free energy, and so on. The selection was easy, especially in view of the general law of equipartition of kinetic energy.

A few words may be said in explanation of this famous law propounded by Maxwell and discussed by practically every student of the theory of gases since that time. In the case in hand, the kinetic energy is a sum $\pi(a_1 p_1^2 + a_2 p_2^2 + a_3 p_3^2)$ of the squares of the momenta and it is clear that the individual terms $\pi a_1 p_1^2$, $\pi a_2 p_2^2$, $\pi a_3 p_3^2$ represent the kinetic energies of the individual gongs. The average value of these partial kinetic energies is easily found. For instance

$$\overline{\pi a_1 p_1^2} = \frac{\int_{-\infty}^{+\infty} \cdots \int \pi a_1 p_1^2 e^{\frac{\psi - \epsilon_p - \epsilon_q}{\Theta}} dp_1 \cdots dq_3}{\int \cdots \int e^{\frac{\psi - \epsilon_p - \epsilon_q}{\Theta}} dp_1 \cdots dq_3}$$

$$= \frac{\int_{-\infty}^{+\infty} \pi a_1 p_1^2 e^{\pi a_1 p_1^2} dp_1 \int \cdots \int e^{\frac{\psi - \pi a_2 p_2^2 - \pi a_3 p_3^2 - \epsilon_q}{\Theta}} dp_2 \cdots dq_3}{\int_{-\infty}^{+\infty} e^{\pi a_1 p_1^2} dp_1 \int \cdots \int e^{\frac{\psi - \pi a_2 p_2^2 - \pi a_3 p_3^2 - \epsilon_q}{\Theta}} dp_2 \cdots dq_3}.$$

Now the integrals though properly iterated, may be considered as merely multiplied: for p_1 does not occur in the last five provided the limits are not taken as functions of p_1. Hence the last five integrals may be canceled from numerator and denominator and the calculation of the simple integrals remaining gives

$$\overline{\pi a_1 p_1^2} = \tfrac{1}{2}\,\Theta.$$

It therefore is seen that the average of each partial kinetic energy corresponding to each individual gong is $\frac{1}{2}\,\Theta$ and the average value of the total kinetic energy is $\frac{1}{2}\,3\Theta$ or $\frac{1}{2}n\Theta$. The fact that each gong has the same average kinetic energy as every other constitutes the law of equipartition of kinetic energy for this particular case. With the proper conventions the same result is obtained for any dynamical system.

The proof that the average kinetic energy in a system of n degrees of freedom is $\frac{1}{2}\,n\,\Theta$ and that each degree of freedom has its aliquot share of the whole depends, as Gibbs gives it, on the assumption of the canonical distribution including the hypothesis that the momenta may have any values between $-\infty$ and $+\infty$ and that the limits of the integrations with respect to the coordinates $q_1, q_2, \cdots, q_n$ do not depend on the momenta. If any of these assumptions were untrue, the proof would not hold. The assumptions seem ideally simple with the exception of the initial assumption of canonical distribution; and at any rate the fact of the at least approximate truth of the law of equipartition of energy is so strikingly confirmed in the theory of gases as to justify the detailed discussion of any reasonable theory which has it as a consequence. This will perhaps serve as an answer to those who might inquire why the particular law of density or probability for the ensemble known as the canonical law was chosen for the work of this article; there are moreover numerous more or less accurate and plausible "proofs" of the law or reasons for it which may be found in various treatises on the theory of gases and in Gibbs's book; but they cannot be taken up here. Other assumptions for the density or probability would have enabled us to compute averages but would in all probability have been destitute of thermodynamic analogy.

Although the general theory of statistical mechanics reached a high development at the hands of Gibbs, the detailed application of the method of investigation to systems that are of thermodynamic importance in physics has scarcely been touched; special methods and approximations for obtaining averages, under the initial assumption not of the canonical distribution but of the law of equipartition of energy, have generally been employed. Indeed it is readily seen that to evaluate an iterated integral like

$$\int_{-\infty}^{+\infty}\cdots\int dp_1\cdots dp_n \int\cdots\int e^{\frac{\psi-\epsilon_p-\epsilon_q}{\Theta}}\,dq_1\cdots dq_n$$

(even where the limits for the integrations with respect to the q's are taken as independent of the p's) is out of the question for most sets of limits and for most assumptions for the potential energy ϵ_q even if the simple assumption be made that the kinetic energy consists of a sum $\Sigma a_i p_i^2$ with constant coefficients. For instance if x_i, y_i, z_i and x_j, y_j, z_j are the coordinates of the centers of two monatomic molecules of a gas, and if the usual law of attraction inversely as the square of the distance and repulsion as the inverse fifth power of the distance be assumed, the potential energy would take the form

$$\epsilon_q = \sum_{i,j}\left[\frac{-a}{\sqrt{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2}} + \frac{b}{(x_i-x_j)^2+(y_i-y_j)^2+(z_i-z_j)^2]^2}\right],$$

to which other terms must be added to keep the molecules within the vessel containing the gas.

Despite the difficulties which seem to lie in the way of the systematic practical application of the statistical mechanics of a canonical distribution of dynamical systems, the fact that the theory leads to the fundamental differential relation of thermodynamics will probably lead to its detailed investigation. It is hoped that the presentation here given may be an aid to those who wish to make a start on this field of science.

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